Spin-split states in aromatic molecules and superconductors

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A state where spin currents exist in the absence of external fields has recently been proposed to describe the superconducting state of metals. It is proposed here that such a state also describes the ground state of aromatic molecules. It is argued that this point of view provides a more natural explanation for the large diamagnetic susceptibilities and NMR shifts observed in these molecules than the conventional viewpoint, and it provides a unified description of aromatic molecules and superconductors as sought by F. London. A six-atom ring model is solved by exact diagonalization and parameters in the model where a ground state spin current exists are found. We suggest that this physics plays a key role in biological matter.

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I. INTRODUCTION

The large anisotropic diamagnetic susceptibility exhibited by aromatic molecules and the associated NMR frequency shifts at nearby atoms are generally interpreted as arising from delocalized ring currents in the molecular rings[1]. This interpretation relies on molecular orbital theory (Huckel theory) of π electrons and assumes electrons are non-interacting[2, 3]. On the other hand, calculations using valence bond theory taking electron-electron interaction into account predict that the π electrons in aromatic rings are localized[4]. These electrons move in a one-dimensional half-filled band, where the effect of electron-electron interactions should be strong; electron-electron interactions in a one-dimensional half-filled band can lead to localization of electrons (Mott insulating state) which would suppress the diamagnetic response. Within valence bond theory the aromatic character is proposed to result from the coupling of electron spins[4].

F. London suggested long ago that the diamagnetic currents in aromatic rings are analogous to supercurrents in superconductors[5]. At that time superconductivity in metals was not understood from a microscopic point of view. After the advent of BCS theory the possible connection between ring currents in aromatic molecules and superconducting currents has been discussed by W. Little[6] in connection with a proposed excitonic pairing mechanism. However, to date no compound has been identified that would exhibit Little's excitonic superconductivity.

The present author suggested in 1990 that the large diamagnetic response of aromatic ring molecules may originate in the existence of a spin current in the ground state of such molecules in the absence of applied fields[7]. Thus, an applied magnetic field would not set electrons into motion but rather slow down the component of the pre-existent spin current in one direction and speed up the spin current in the opposite direction. A heuristic model for this physics was proposed and it was suggested that it provides a natural explanation for various experimental observations. At that time we did not make a connection between this physics and superconductivity.

However our recent work on the theory of hole superconductivity[8] led to the conclusion that metals expel negative charge from the interior towards the surface in the transition to the superconducting state[9]. This phenomenon (which also provides a 'dynamical' explanation of the Meissner effect[10]) leads to the prediction that a a macroscopic spin current exists near the surface of superconductors in the absence of applied external fields (Spin Meissner effect)[11, 12]. Naturally this raises the question whether the spin currents in aromatic molecules proposed in ref.[7] are related to the spin currents in superconductors recently predicted[12]. In this paper we propose that in fact such a deep connection exists, validating the early intuition of F. London. A state qualitatively different from the Huckel[2, 3] and valence bond[4] states, carrying a spin current around the ring, is proposed to describe the ground state of aromatic molecules.

II. SPIN CURRENT AND π FLUX IN SUPERCONDUCTORS

We have recently proposed that the Meissner effect in superconductors can be understood 'dynamically' if electrons expand their orbits to mesoscopic orbits of radius $2\lambda_L$ in the transition to superconductivity, with λ_L the London penetration depth[12]. In the absence of applied magnetic field this orbit expansion results, through the spin-orbit interaction of the electron magnetic moment $\mu_B = e\hbar/2m_e c$ with the positive ionic background $|e|n_s$ (n_s =superfluid density), in a spin current with speed[12]

$$v_\sigma^0 = \frac{\hbar}{4m_e\lambda_L} \tag{1}$$

and opposite direction for electrons with opposite spin.

The angular momentum of electrons in orbits of radius $2\lambda_L$ with speed Eq. (1) is

$$L = m_e v_\sigma^0(2\lambda_L) = \frac{\hbar}{2} \tag{2}$$

This remarkable result indicates that electrons in superconductors have an orbital 'spin' analogous to the intrinsic electron spin. A spinning electron can be visualized as a charge orbiting at speed c in a circle of quantum electron radius

$$r_q = \frac{\hbar}{2m_e c} \qquad (3)$$

and the electron in the superconductor can be interpreted as an 'amplified image' of the spinning electron, with amplification factor $2\lambda_L/r_q$[13].

An angular momentum $\hbar/2$ corresponds to a wavefunction $\Psi = |\Psi|e^{i\theta}$ depending on the azimuthal angle φ as

$$\Psi \propto e^{i\theta(\varphi)} = e^{\pm i\varphi/2} \qquad (4)$$

so that the electron acquires a phase π in traversing a full orbit. This in turn can be understood as arising from a 'flux' ϕ_0 inside the orbit giving rise to the phase factor

$$e^{\frac{ie}{\hbar c}\oint \vec{A}_\sigma \cdot \vec{dl}} = e^{\frac{ie}{\hbar c}\sigma\phi_0} = e^{\pm i\pi} \qquad (5)$$

with $\phi_0 = \frac{hc}{2e}$ the flux quantum and A_σ the spin-orbit vector potential[14].

Thus, the development of the macroscopic spin current predicted by the theory of hole superconductivity upon the establishment of macroscopic phase coherence in superconductors requires 'closing'[15] of the wavefunction for each member of the Cooper pair according to the relation

$$\oint \vec{\nabla}\theta_\sigma \cdot \vec{dl} = \pm\pi \qquad (6)$$

where θ_σ is the phase of the member of the Cooper pair of spin σ, instead of the usual Bohr-Sommerfeld quantization rule. Alternatively we can think of θ_σ as characterizing the phase of the entire condensate of spin σ rather than a single member of a Cooper pair, since the phases of different Cooper pairs are phase locked due to macroscopic phase coherence. The phase factor $e^{\pm i\pi} = -1$ acquired by one spin component is cancelled by the same factor in the opposite spin component so that the superconducting wavefunction is single-valued.

As is well known, for an individual spin-1/2 spinor, a rotation by 360 degrees gives rise to a change in sign[16], which we can also interpret as arising from an enclosed $\pi-$flux. Thus, a single spinning electron shows the same phase behavior as the Cooper pair member in the mesoscopic orbits in the superconductor within the theory of hole superconductivity, proposed to describe all superconductors[17]. The fact that the same physics shows up at the subatomic scale r_q (Eq. (3)) and at the mesoscopic scale $2\lambda_L$ suggests that it will also show up at other length scales provided phase coherence exists. In this paper we propose that this physics shows up at the atomic scale $a_0 = \hbar^2/m_e e^2 \sim \sqrt{r_q(2\lambda_L)}$ and in particular manifests itself in the existence of a spin current in the ground state of aromatic molecules such as benzene.
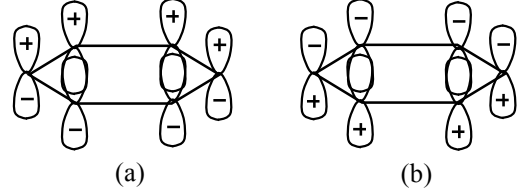

FIG. 1: The two possible orientations of the carbon p_z orbitals in the benzene molecule. In the conventional point of view only one of them (either one) plays a role.
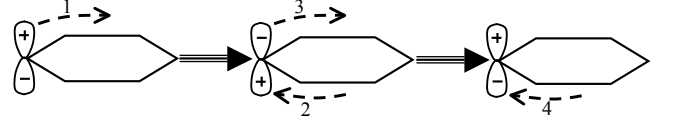

FIG. 2: In the point of view proposed here, as the electron goes around the benzene ring once, it ends up in the orbital with opposite sign. Two rounds are needed to go back to the original state.

III. SPIN CURRENT AND π FLUX IN BENZENE

The aromatic character of benzene is ascribed to the six electrons in the $p\pi$ orbitals oriented perpendicular to the plane of the molecule. There are two possible orientations for the atomic wave function, as shown schematically in Fig. 1. In the conventional point of view, these two orientations are equivalent except for a sign convention which has no physical significance, and either one of them is used. Instead, we propose here that the fact that there are two possible orientations of the p_z orbital as shown in Fig. 1 *has profound physical significance*.

We propose, by analogy with the situation for the intrinsic electron spin[16], as well as for the $2\lambda_L$ orbits in the superconductor discussed in the previous section, that as an electron goes around once in the aromatic ring, it ends up in the orbital with opposite sign orientation, as shown schematically in Figure 2. That is, the electron acquires a π phase shift, and two rounds are needed to bring the electron back to its original state with the same sign. Because for every spin-up electron there is a spin-down electron moving around in opposite direction, no sign change occurs for the wavefunction of the system as a whole, just like in the case of the superconductor.

To describe this scenario we may take the tight binding Hamiltonian kinetic energy with hopping between nearest neighbors $<ij>$

$$H_{kin} = -\sum_{<ij>\sigma} t_{ij}(c_{i\sigma}^\dagger c_{j\sigma} + h.c.) \qquad (7)$$

and take hoppings $t_{ij} = t$ for all bonds except one, where $t_{ij} = -t$, corresponding to 'antiperiodic' boundary conditions. Thus, the electrons acquire a phase π in going around the ring. The non-interacting spectrum and the
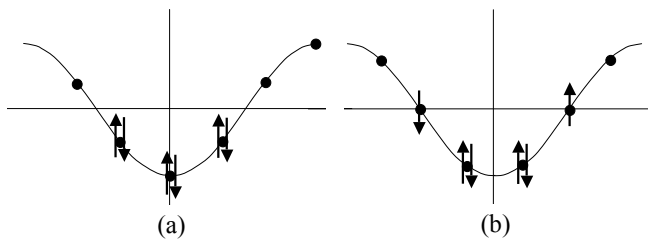
FIG. 3: In the conventional scenario (a), the ground state of benzene is non-degenerate and there is no spin current. In the scenario proposed here (b) the (non-interacting) ground state is four-fold degenerate and can carry spin current.
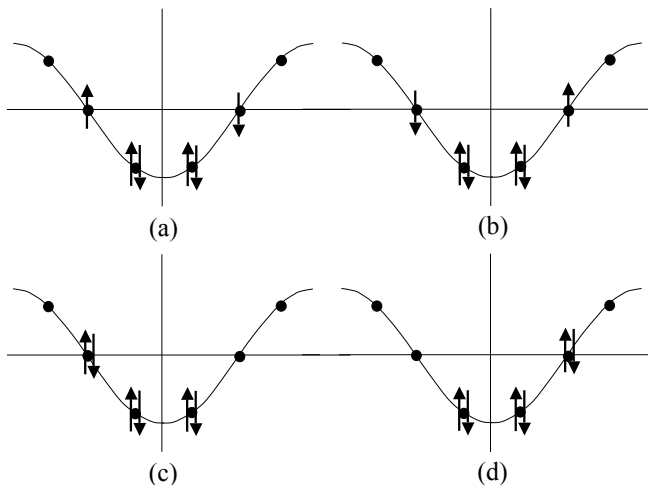

FIG. 4: In the scenario proposed here, the non-interacting ground state is four-fold degenerate as shown in the Figure. Two of the ground states, (a) and (b), carry spin current and the other two, (c) and (d), carry charge current.

occupation of the states for 6 electrons is shown in Fig. 3 contrasted with the conventional case. In the scenario considered here there are four degenerate ground states in the non-interacting case, shown in Fig. 4. Two of them carry a spin current.

The energy level structure shown in Fig. 4 would arise within the conventional viewpoint if there is an applied magnetic field with flux ϕ_0 within the aromatic ring. Here we propose that this structure arises spontaneously in benzene in the absence of applied magnetic field. It can be thought of as arising from $\pi - f$ lux of opposite sign affecting the states of up and down electrons and parallels the behavior predicted for superconductors by the theory of hole superconductivity[12].

Alternatively we argue as follows. Consider a rotation of the coordinate system by an angle $\varphi = \pi/3$ around the $z-$axis chosen perpendicular to the plane of the aromatic ring. This is a symmetry operation that leaves the benzene ring invariant. A spinor χ localized at a given atom in the ring is described in the new coordinate system by

the spinor[16]

$$\chi' = e^{-i\frac{\varphi}{2}\hat{n}\cdot\vec{\sigma}}\chi \equiv e^{-i\theta\sigma_z}\chi, \qquad (8)$$

with $\theta = \pi/6$. Six such transformations in sequence bring the coordinate system back to the original one, however the spinor changes its sign. We now consider these symmetry operations from an "active" rather than a "passive" point of view. Namely, instead of rotating the observer's coordinate system we rotate our physical system, the spinor. If χ is an eigenstate of σ_z, it acquires a phase factor $e^{\pm i\pi/6}$ in hopping from a site to a neighboring site, with opposite sign phase factor for both eigenstates of σ_z.

Adopting this point of view, the kinetic energy operator is, instead of Eq. (7)

$$H_{kin} = -\sum_{<ij>\sigma}[t_{ij}^\sigma c_{i\sigma}^\dagger c_{j\sigma} + h.c.] \qquad (9a)$$

$$t_{ij}^\sigma = te^{i(i-j)\theta_\sigma} \qquad (9b)$$

$$\theta_\sigma = \frac{\pi}{6}\sigma \qquad (9c)$$

and the spin quantized in direction perpendicular to the plane of the molecule. The energy spectrum is identical to that shown in Figure 4. In Eq. (9a), $< ij >$ indicates nearest neighbor atoms with i to the left of j.

IV. ELECTRON-ELECTRON INTERACTIONS

Can states that carry a spin current, such as those shown in Fig. 4 (a) and (b), be stable in the presence of strong electron-electron interactions? It may be suspected that in a finite ring electron-electron scattering will destroy the spin current by coupling states with spin current flowing in opposite directions[18].

We consider the kinetic energies Eq. (7) or (9) in the presence of on-site and nearest neighbor Coulomb repulsion as well as nearest neighbor ferromagnetic exchange

$$
\begin{aligned}
H = {} & H_{kin} + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{<i.j>\sigma} n_i n_j \\
& + \sum_{<i.j>\sigma\sigma'} J_{ij}^{\sigma\sigma'} c_{i\sigma}^\dagger c_{j\sigma} c_{j\sigma'}^\dagger c_{i\sigma'}
\end{aligned} \qquad (10)
$$

With the kinetic energy Eq. (7) we have simply $J_{ij}^{\sigma\sigma'} = J > 0$. This term (ferromagnetic nearest neighbor exchange term) arises from an off-diagonal matrix element of the Coulomb interaction in the tight binding formulation (J) which is always positive[19]. It was proposed in Ref.[7] that it plays an essential role in stabilizing the spin-split state in aromatic molecules. However, in Ref.[7], the spin current state envisioned was based on excitations of the conventional non-interacting system Fig. 3(a). We find here that J also plays an essential role in
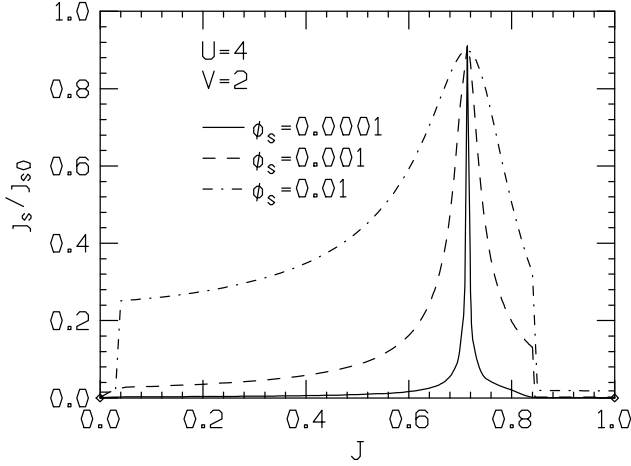
FIG. 5: Spin current versus nearest neighbor ferromagnetic exchange interaction strength for three values of the staggered flux ϕ_s in Eq. (12).

stabilizing the spin current state based on the scenario of Fig. 4. If we use the kinetic energy Eq. (9), the J interaction in Eq. (10) takes the form

$$J_{ij}^{\sigma\sigma'} = J e^{i(i-j)(\theta_\sigma - \theta_{\sigma'})} \tag{11}$$

so that it acquires a phase factor for exchange of electrons of opposite spin. The spectrum of the Hamiltonian Eq. (10) is the same for the two forms of the kinetic energy Eq. (7) and Eq. (9) and we will use Eq. (9) in what follows.

We diagonalize the Hamiltonian Eq. (10) exactly for 6 electrons with equal number of up and down spins. It is easy to see that in the presence of interactions the ground state cannot carry a spin current if it is non-degenerate, since such a spontaneously broken symmetry state cannot exist in a finite system. So we look for parameters in the Hamiltonian that will give rise to a doubly degenerate or nearly doubly degenerate ground state. Indeed we find that generically such Hamiltonian parameters exist even for the case of strong interactions. We find them in the neighborhood of $U \sim 2V$ and they require non-zero values of the exchange interaction J.

Consider for example the case $U = 4$, $V = 2$ (with $t = 1$). To detect a spin current we add to the phases of the spinors a small staggered flux ϕ_s, i.e. take

$$\theta_\sigma = (\frac{\pi}{6} + \phi_s)\sigma. \tag{12}$$

This arises in the real system from the spin-orbit interaction not included in the Hamiltonian Eq. (10), as discussed in the next section. Figure 5 shows the ground state spin current

$$j_s = \frac{1}{2}(<j_\uparrow> - <j_\downarrow>) \tag{13}$$

with

$$j_\sigma = -i(t_{ij}^\sigma c_{i\sigma}^\dagger c_{i+1,\sigma} - h.c.) \tag{14}$$
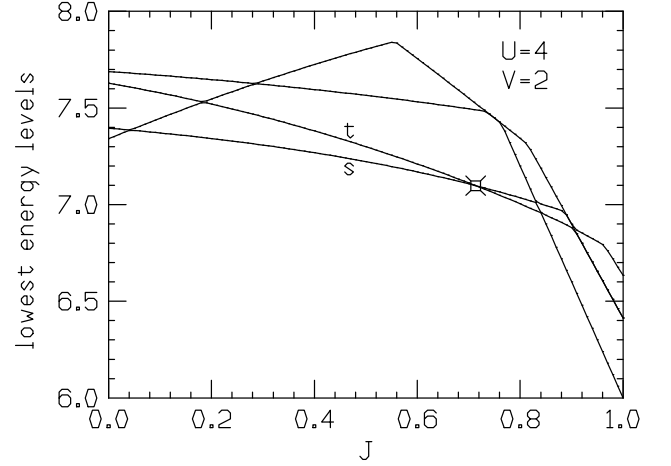

FIG. 6: Four lowest energy levels of the Hamiltonian for $U = 4$, $V = 2$ as function of J. The ground state switches from singlet (s) to triplet (t) at $J \sim 0.714$. At that point (indicated by the symbol in the figure) the degenerate ground state corresponds to the spin-current carrying states of Fig. 4 (a), (b).
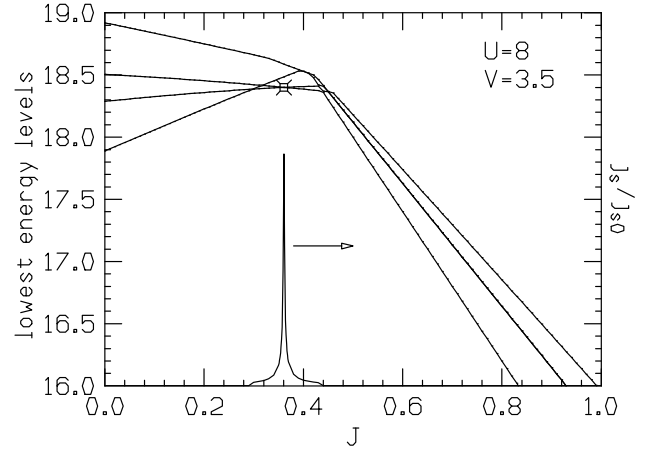

FIG. 7: Four lowest energy levels of the Hamiltonian for $U = 8$, $V = 3.5$ as function of J. The singlet-triplet crossing point where the spin current is largest is at $J \sim 0.361$.

versus the nearest neighbor exchange amplitude J for three small values of the staggered flux ϕ_s. It can be seen that a spin current exists for finite staggered flux and non-zero J. As the staggered flux approaches zero, the spin current approaches a $\delta-$function at one value of J, $J = 0.714$ for this case. This corresponds to the crossing of the two lowest energy levels, a singlet and a triplet, as shown in Fig. 6. In the limit $\phi_s \to 0$, spin current will only exists at the precise point where the energy levels cross.

Similarly we show in Figs. 7 and 8 the four lowest energy levels and the ground state spin current for symmetry-breaking field $\phi_s = 0.0001$ for two other sets of U, V values. It can be seen that the behavior is generic.
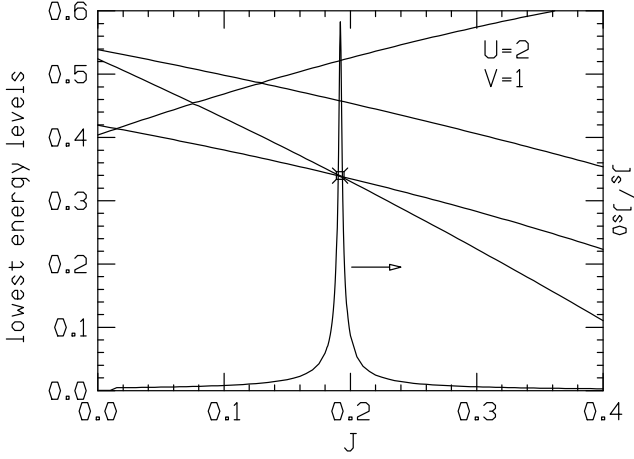
FIG. 8: Four lowest energy levels of the Hamiltonian for $U = 2$, $V = 1$ as function of J. The singlet-triplet crossing point where the spin current is largest is at $J \sim 0.192$.
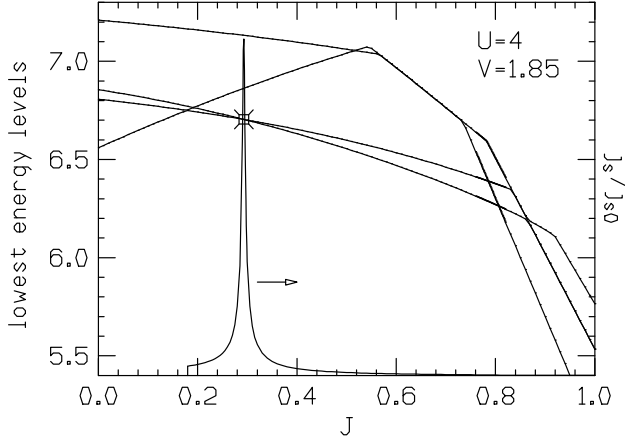

FIG. 9: Four lowest energy levels of the Hamiltonian for $U = 4$, $V = 1.85$ as function of J. The singlet-triplet crossing point where the spin current is largest is at $J \sim 0.293$.

Note that the range of parameters in the model where we find this interesting behavior is quite reasonable. For example, first principles calculations for benzene yield values $t = 2.40 eV$, $U = 11.26 eV$[21]. The nearest neighbor repulsion V estimated from the Ohno formula[22] $V(R) = U/\sqrt{1 + R^2 U^2/e^4}$ yields $V = 7.6 eV$ for nearest neighbor distance $R = 1.4 A$. Hence $U/t = 4.7$, $V/t = 3.2$. The estimation of these parameters is subject to ambiguity, for example related to the validity of the zero differential overlap approximation[20]. Furthermore the parameter values could be renormalized by inclusion of further neighbor interactions in the model. We will investigate these questions in separate work.

The range of nearest neighbor interaction values where this behavior occurs is rather restricted. Fig. 9 shows the lowest energy levels for $U = 4$, $V = 1.85$. The crossing point where spin current exists for infinitesimal spin-orbit
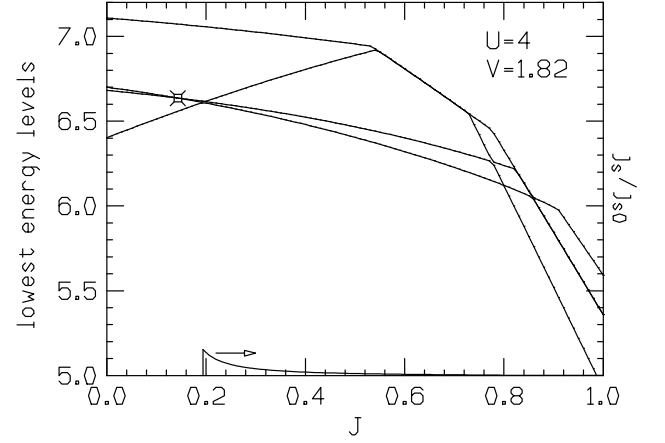
FIG. 10: Four lowest energy levels of the Hamiltonian for $U = 4$, $V = 1.82$ as function of J. The singlet-triplet crossing point is at $J \sim 0.143$ indicated by the symbol in the figure, however another singlet energy level lower in energy exists for that J that does not carry a spin current.
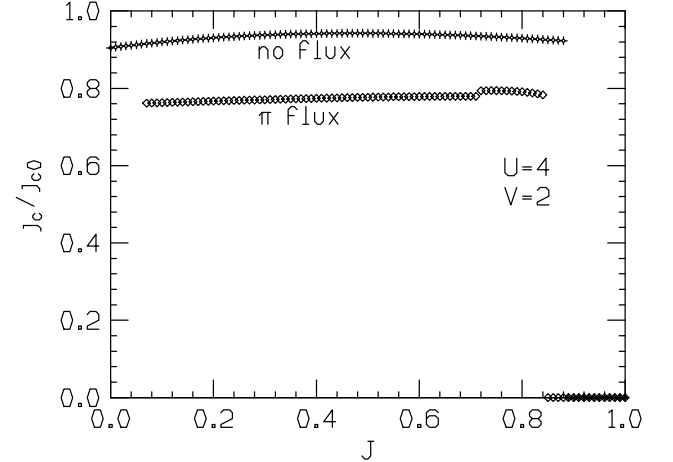

FIG. 11: Charge current response to applied magnetic field relative to non-interacting case with periodic boundary condition, for the case $U = 4$, $V = 2$. The conventional scenario (no flux) gives somewhat larger charge current than the scenario proposed here. The small kink in the $\pi-$ flux case near $J = 0.7$ corresponds to the energy level crossing point in Fig. 6.

coupling has moved from $J = 0.714$ down to $J = 0.293$. For smaller V the crossing point for these energy levels moves further to the left and crosses another energy level, that becomes the lowest energy state and does not carry spin current, as shown in Fig. 10 for $U = 4$, $V = 1.82$. However even in this situation if the spin-orbit interaction is finite the ground state and first excited state will carry a spin current for J larger than the crossing point with the non-spin-current carrying ground state ($J > 0.2$ in Fig. 10).

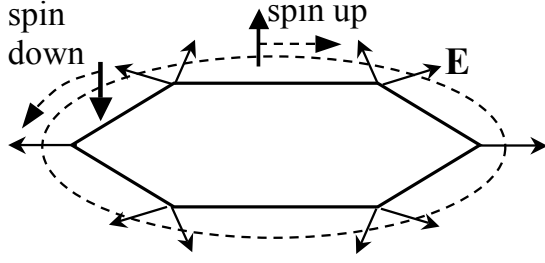Thus, for $U = 4$ the range of V where a spin cur-

FIG. 12: Electrons move in an outward-pointing electric field **E** originating in the charge transfer from the C atom to the $C-H$ bond. The spin down (up) electron has lower energy when orbiting counterclockwise (clockwise), as shown in the figure, due to spin-orbit coupling.

rent carrying ground state for an infinitesimal ϕ_s exists is restricted to $1.83 \leq V \leq 2.05$. Similarly restricted parameter ranges where spin current in the ground state can develop for infinitesimal spin-orbit coupling exist for other U values.

The response of the system to an applied external magnetic field is similar to the conventional scenario for the case considered here. Figure 11 shows the charge current that develops for the case $U = 4$, $V = 2$ as function of J, relative to the current expected within Huckel theory (non-interacting electrons) in the presence of a small magnetic flux, of the same sign for both spin orientations. Both the conventional scenario with no spin-orbit flux and the scenario with $\pi-$flux proposed here give a charge current, hence a diamagnetic susceptibility, that is almost constant as function of the interaction J and not much smaller than the non-interacting value (which is 1 in Fig. 11). The small glitch in the lower curve corresponds to the point where the energy level crossing occurs in Fig. 6.

V. SPIN-ORBIT COUPLING

If the ground state of the interacting Hamiltonian is degenerate (or nearly degenerate) in the way discussed in the previous section, spin-orbit coupling will split the degeneracy and give rise to two spin-current-carrying low-lying states. The lowest of the two states is shown schematically in Fig. 12.

We can understand the physics as follows. The electron in the spin current moves in an electric field pointing outwards, just like in an atom or in the superconductor according to the theory of hole superconductivity[12]. The spin-orbit interaction Hamiltonian in electric field $\vec{E}$ is

$$H_{so} = -\frac{e\hbar}{4m_e^2c^2}\vec{\sigma} \cdot (\vec{E} \times \vec{p})$$ (15)

and it gives rise to an energy splitting

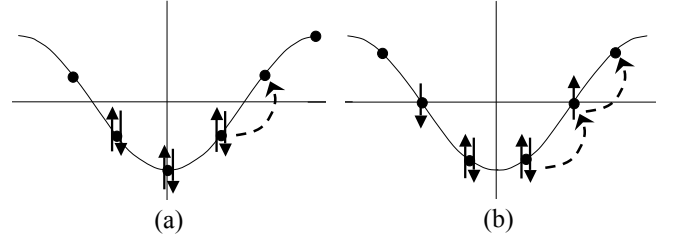$$\Delta E = \frac{e\hbar}{2m_e^2c^2}Ep$$ (16)

FIG. 13: Allowed optical transitions in benzene in the conventional scenario ((a)) and in the scenario proposed here ((b)) are indicated by the dashed lines.

between electrons with spin parallel and antiparallel to $\vec{E} \times \vec{p}$. Taking $p \sim \hbar/a$, with a the radius of the orbit (or equivalently the $C-C$ distance)

$$\Delta E = \frac{e\hbar^2}{2m_e^2c^2a}E$$ (17)

The spin-orbit interaction gives rise to the Aharonov-Casher vector potential[23]

$$\vec{A}_\sigma = \frac{1}{2e}\vec{\mu} \times \vec{E}$$ (18)

with $\vec{\mu} = \mu_B\vec{\sigma}$, μ_B the Bohr magneton. In going around the ring the electron acquires a phase shift

$$\delta\theta_{AC} = \frac{e}{\hbar c}\oint A_\sigma \cdot dl = \frac{2\pi a e}{\hbar c}A_\sigma = \frac{\pi a e}{2m_e c^2}E$$ (19)

or in terms of the energy splitting Eq. (17)

$$\delta\theta_{AC} = \frac{m_e}{\hbar^2}\pi a^2\Delta E$$ (20)

Assuming the energy splitting ΔE is given by the atomic spin-orbit splitting in C between $^2P_{3/2}$ and $^2P_{1/2}$ states, $\Delta E = 8 meV$, gives for the AC phase Eq. (20) $\delta\theta_{AC} = 0.065$. The staggered flux introduced in Eq. (12) is then 1/6th of this value, i.e.

$$\phi_s = 0.0011$$ (21)

close to the middle value of ϕ_s used for illustration in Fig. 5. For spin-orbit energy splitting a factor of 10 larger, i.e. $\Delta E \sim 80 meV$, the flux corresponds to the largest value shown in Fig. 5, where a rather large spin current occurs in a wide range of J values.

In summary, we propose that the two lowest energy states of benzene carry a large spin current around the ring, as depicted schematically in Fig. 4 (a) and (b), and have a small energy separation of order meV. The ground state has spin current direction as shown in Fig. 12.

VI. PHYSICAL CONSEQUENCES

One immediate consequence of the scenario proposed here concerns optical properties and is illustrated in Fig.

13. As discussed by Platt[24], allowed optical transitions in benzene require change of one unit of angular momentum, corresponding to change of the electron wave vector by $2\pi/6$. In the conventional scenario there is only one way to do this starting from the ground state, as shown schematically in Fig. 13 (a). In the scenario proposed here there are two distinct ways of exciting electrons to states differing in wave vector by $2\pi/6$, as shown in Fig. 13 (b). The photon wavelengths associated with these two processes should be different because of the different effects of electron-electron interactions in the final states.

Experimentally[25] three bands are seen in the optical absorption spectrum of benzene, at wavelengths around $\lambda = 2600A$, $2050A$ and $1850A$. The one at 2600 is weak and has considerable fine structure, thus it is likely to arise from 'forbidden transitions' involving interaction with vibrational degrees of freedom[26]. The other two bands are much stronger, and their interpretation has been controversial, because there is only one allowed transition in the conventional scenario (Fig. 13(a)). There is general agreement that the transition at $\lambda = 1850A$ is an allowed one because it is the strongest, and the transition at $\lambda = 2050A$ has been attributed to one or another forbidden transition. A variety of calculations of oscillator strength have been reported[27–30] but it is not clear that these complicated calculations explain the experimental observations. Instead, our scenario predicts two allowed transitions (Fig. 13(b)) and hence two strong absorption bands in the optical absorption of benzene, thus offering the possibility of a more natural explanation for the observations.

The ground state and low-lying energy state proposed here for benzene are neither pure singlet nor triplet, instead singlet and triplet are strongly mixed, with nearly equal weights if J is near the crossing point of singlet and triplet energy levels shown in the figures. It is possible that transitions from higher excited states to these states will provide a more natural explanation of the phosphorescence properies of benzene than the conventional understanding, within which phosphorescence in benzene is 'doubly forbidden' and requires vibronic interactions to play a key role[31].

The spin current proposed to exist in benzene will give rise to an electric field[7]. A moving magnetic moment $\vec{\mu}$ is equivalent to an electric dipole moment $\vec{p}$ in the laboratory frame

$$\vec{p} = \frac{\vec{v}}{c} \times \vec{\mu} \tag{22}$$

and will give rise to an 'effective' dipolar charge distribution depicted schematically in Fig. 14. This dipolar charge distribution generates a quadrupolar electric field around the aromatic ring. For a point in the plane at distance $x >> a$ from the center of the ring

$$E(x) \sim \frac{6pa}{x^4} \tag{23}$$

with a the radius of the ring. At distance $x = 2a$ of the center, the electric field is $E \sim p/a^3$. From Eq. (22)
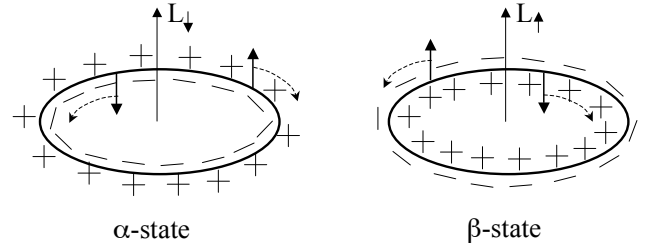

FIG. 14: Dipolar charge distribution produced by spin current. α−state: spin antiparallel to orbital angular momentum, β−state: spin parallel to orbital angular momentum. L_σ denotes the orbital angular momentum for spin σ and only the upward pointing L_σ is shown. The α−state will generally be lower in energy due to spin-orbit coupling.

the dipole moment is $p \sim 77\mu V A^2$ for benzene, and the magnitude of the electric field at $x = 2a$ is $E \sim 54\mu V/A$.

We suggest that the two low-lying states of the aromatic ring depicted in Fig. 14, which we call α and β states, are stable, because of the topological constraint that the 'winding number' for electrons going around the ring is $1/2$, and that a large energy barrier exists for switching between α and β states. If these states exist in aromatic rings they are likely to play a crucial role in biological matter where aromatic rings are ubiquitous.

How can an aromatic ring 'switch' from one to the other low-lying state? The β state becomes the lower energy state if the electric field that the electrons in the spin current 'see' points inward rather than outward, which could occur upon changes in the electrostatic field around the ring caused by chemical reactions involving charge transfer, or transport of ions or electrons. A proton going through the interior of a benzene ring[32] may switch a β to an α configuration due to the additional strong electric field pointing outward, and conversely an electron going through the center of a benzene ring may switch the α to the β state.

It is tempting to speculate that the α and β states could act as quantum qubits in a topological quantum computer[33], namely the brain. Electric fields originating in the spin current, of the magnitude estimated above, and resulting electric potential differences may be involved in neural signal transmission. Or, the α and β states in aromatic rings in the brain may just be storing one classical bit of information and play a key role in memory storage[7]. Phase coherence of spin ring currents over large distances could play an important role in various aspects of brain activity such as sleep. More generally, these stable dynamic low-lying states of aromatic rings may play a key role in a wide variety of biological processes in living organisms[34].

As discussed earlier, the theory of hole superconductivity predicts that superconductors in the ground state also carry a spin current and associated π flux. The ground state of a small superconducting ring corresponds to the α state in Fig. 14. It should be possible to switch such a

ring to the β state, perhaps through transient application of a large electrostatic field or a very large magnetic field. Such ring would exhibit a stable persistent spin current in opposite direction to that of the ground state (in the absence of external fields), and experimental detection of such a state would provide convincing proof of the theory discussed here and in ref.[12]. The existence of such spin currents in superconducting rings could be experimentally demonstrated by detection of the quadrupolar electric fields generated by the dipolar charge distributions shown in Fig. 14, or by measuring the resulting force between small superconducting rings with spin currents, as discussed in ref.[12].

VII. DISCUSSION

Aromatic rings have $4n + 2$ atoms, with n integer. It is generally believed that such molecules have a singlet ground state described by delocalized electrons in a half-filled band[2, 3], with a large energy gap to the first excited state. Alternatively, it has been proposed that a similar energy level structure and aromatic character can be described by a valence bond state with localized electrons and coupling between electron spins[4]. In this paper we have proposed instead a qualitatively different scenario: that the ground state of aromatic ring molecules is a mixture of singlet and triplet states that carries a spin current around the ring, and that another such state exists nearby in energy carrying spin current in the opposite direction. We have also proposed that the same is true for small superconducting rings made of ordinary superconductors.

This scenario follows from the fundamental assumption that when an electron goes around a closed path in a coherent way it acquires a π phase shift, and two rounds are needed to bring it back to the original state, like a

point in a Moebius strip. In the aromatic ring, starting in a p_z orbital the electron ends up in the $(-p_z)$ orbital after one round. We have justified this assumption by invoking the transformation properties of the spinor under rotation in quantum mechanics[16], and by analogy with the phase behavior predicted by the theory of hole superconductivity, stemming from the finding that electrons in a Cooper pair carry orbital angular momentum $\hbar/2$[12].

Within this assumption, and using a Hubbard-like Hamiltonian including nearest neighbor exchange to model the benzene ring, we have found reasonable parameter ranges in the interacting system where a spin-current-carrying ground state and low-lying excited state exists. The same is likely to be true for other aromatic ring structures using the same model. We have argued that our scenario provides a more natural explanation for the optical properties of benzene as well as for the existence of ring currents evidenced by its large diamagnetic susceptibility and proton NMR shifts.

Whether our proposal is true or false can be decided experimentally. It should be possible to make aromatic rings and small superconducting rings in both predicted low-lying spin current states and study their properties.

If our proposal is true it is likely to yield fundamental insights into the properties of biological matter, as well as on quantum mechanics itself, changing the currently accepted understanding in fundamental ways. It is also likely to open up possibilities of qualitatively new technological advances such as quantum computation.

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